

(1.16 mole) of methylamine in 400 ml. of dry benzene between 5° and 10°. After addition was completed, the mixture was allowed to warm to room temperature and stand overnight. The methylamine hydrochloride was removed by filtration and the benzene distilled from the filtrate under reduced pressure. The residue was distilled under reduced pressure. Some deamination occurred during distillation with the release of dimethylamine. Crystals formed in the distillate and were separated by filtration. The filtrate, 39 g. was pentamethylphosphoric triamide.

The crystalline material was washed with ether and could not be further purified. This product is believed to be trimethylphosphoramidate.

Mol. wt. 242 determined ebullioscopically⁸ in benzene.

N,N'-Dimethyl-*P*-trichloromethylphosphonic diamide. Methylamine, 40 g. (1.28 moles), in 500 ml. of chloroform was cooled to 2° and trichloromethylphosphonic dichloride⁹ 75 g. (0.32 mole), in 100 ml. chloroform was added dropwise with stirring below 8°. The mixture was stirred for 1 hr. after addition was complete and then allowed to warm to room temperature. The methylamine hydrochloride was removed by filtration and the chloroform distilled from the filtrate under reduced pressure. The residue was recrystallized from benzene yielding 27 g. of *N,N'*-dimethyl-*P*-trichloromethylphosphonic diamide, m.p. 122–124°. Recrystallization from water raised the m.p. to 133–135°.

Thermal deaminations. A sample, 20 g., of the amides listed below was heated at 200–250° under vacuum until a weight loss equal to one equivalent of methylamine was observed. This required 4 to 8 hr. of heating. *N,N',N''*-Trimethylphosphoric triamide yielded a resinous solid.

Anal: Calcd. for C₆H₇N₃OP: N, 26.4.

Found: N, 26.2. Mol. wt. 301, determined ebullioscopically⁸ in methanol.

N,N',N''-Trimethylphosphorothionic triamide yielded a crystalline solid which was recrystallized from toluene.

Mol. wt. 244, determined ebullioscopically in benzene. (See Table I.)

(8) A. W. C. Menzies and S. L. Wright, Jr., *J. Am. Chem. Soc.*, **43**, 2314 (1921).

(9) K. C. Kennard and C. S. Hamilton, *J. Am. Chem. Soc.*, **77**, 1156 (1955).

Ethyl *N,N'*-dimethylphosphorodiamidate yielded a resinous-like material.

Anal: Calcd. for C₄H₈NO₂P: N, 11.6. Found: N, 15.5.

Diethyl *N*-methylphosphoramidate did not diaminate at 250°.

Reactions of sodium salts. Diethyl *N*-methylphosphoramidate,^{6,10} 27 g. (0.15 mole), was dissolved in 100 ml. of dry benzene and 3.5 g. (0.15 mole) of sodium sand was added. There was a slight temperature rise and the evolution of hydrogen. Warming the mixture to 50° was necessary to completely dissolve the sodium. The solution was added to epichlorohydrin, 14 g. (0.15 mole), and the mixture stirred for 1 hr. at 50°, then allowed to stand overnight at room temperature. The solution was decanted off leaving a gummy residue. The solvent was removed under vacuum from the decanted solution, and the residue distilled under reduced pressure, yielding 13.0 g. (40%) diethyl *N*-methyl-*N*-(2,3-epoxypropyl)phosphoramidate.

A similar preparation using 30.4 g. (0.2 mole) ethyl *N,N'*-dimethylphosphorodiamidate, 9.2 g. (0.4 mole) sodium sand, and 20 g. (0.2+ mole) epichlorohydrin yielded 4.6 g. unreacted sodium and 34 g. of undistillable oil.

Anal: Calcd. for C₇H₁₇N₂O₃P: Oxirane oxygen 7.8. Found: Oxirane oxygen¹¹ 6.6.

An attempted preparation of diethyl *N*-benzyl-*N*-methylphosphoramidate by the reaction of equimolar quantities of diethyl-*N*-methyl phosphoramidate, sodium sand, and benzyl chloride by this procedure yielded only 1 g. of product. B.p. 110–119° (1 mm.).

Anal: Calcd. for C₁₂H₂₀NO₂P: N, 5.45. Found: N, 5.35.

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(10) H. McCombie, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 921 (1945).

(11) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF TULANE UNIVERSITY]

Pyrolysis of Thiophene¹

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Pyrolysis of thiophene at 850° gives a mixture of the three isomeric bithiophenes in 7–8% conversion. Mass spectral analysis of the pyrolyzate furnishes evidence for the occurrence of a variety of additional condensation products.

In 1894 Auwers and Bredt² published a brief study on the isolation of two crystalline fractions, m.p. 44–48° and 127–128°, respectively, from the pyrolyzate when thiophene was passed through a tube at "cherry-red" heat. In view of the proximity of these melting points as well as those of the derived bromides to those reported for authentic 2,2'- and 3,3'-bithiophene, the authors concluded that these compounds were present in their crystal-

line pyrolyzate. Inspection of the data in Table I appears to confirm these conclusions.

We have now reinvestigated the pyrolysis of thiophene, and have found that passage through a Vycor glass tube at 800–850° converts 40% of the thiophene into other products. Table II contains the results of the initial fractionation of this crude pyrolyzate.

Fraction I could be separated into an oily fraction A (38%) and a crystalline fraction B (55%) by repeated sublimation. Mass spectral analysis, as well as the infrared and ultraviolet spectra of frac-

(1) This work was supported by the office of Ordnance Research, Contract Number DA-01-009-ORD-500.

(2) K. Auwers and T. V. Bredt, *Ber.*, **27**, 1741 (1894).

TABLE I
IDENTIFICATION OF BITHIOPHENES IN PYROLYZATE

Compound	M.P., °C.	Auwers' work	Our work
2,2'-Bithiophene	33 ³	44-48	Oil
2,3'-Bithiophene	65 ⁴		62-63
3,3'-Bithiophene	133 ²	127-128	132-133
5,5'-Dibromo-2,2'-bithiophene	143 ²		146.0-146.5
3,3',4,4',5,5'-Hexabromo-2,2'-bithiophene	257 ²	249	

TABLE II
DISTRIBUTION OF CRUDE PRODUCTS IN PYROLYZATE

Product	%
Carbon disulfide	15
Carbon	10
Hydrogen sulfide	4
Oil volatile in steam, fraction I	14
Oil nonvolatile in steam, fraction II	34
Volatile gases, losses	22

tion IA indicated that it was composed of thianaphthene (60%) and bithiophenes (25%). Traces of naphthalene, phenylthiophenes, and thiophthenes may also have been present in this fraction on the basis of its mass spectrogram. Spectral analysis of solid fraction IB indicated the presence of bithiophenes (85%) and phenylthiophenes (8%) as the major constituents. Traces of benzothiophene also appeared to be present. By a combination of chromatography and fractional crystallization it was possible to isolate two fractions, m.p. 61.5-62.8° and 132.5-133.2°. These were identified as 2,3'-bithiophene and 3,3'-bithiophene, respectively, by mixture melting point determinations with authentic specimen. From the mother liquors a small amount of material melting at 42-44° was isolated to which the 2-phenylthiophene structure was tentatively assigned, while an oil remained which could be converted to the known² 5,5'-dibromo-2,2'-bithiophene, m.p. 146.0-146.5° undepressed on admixture with an authentic sample. These data are summarized in Table I.

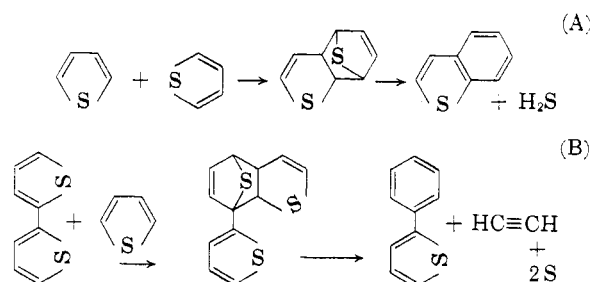
Although it might be assumed that under the conditions of this pyrolysis almost any type of fragmentation and recombination could occur, a rational pathway appears to suggest itself for many of the products of this reaction.

If the assumption is made that self-addition of the Diels-Alder type is possible and that aromatization of the adducts prevents reversal of this reac-

(3) W. Steinkopf, R. Leitsmann, and K. H. Hoffman, *Ann.*, **546**, 180 (1941); J. W. Sease and L. Zechmeister, *J. Am. Chem. Soc.*, **69**, 270 (1947); C. D. Hurd and K. L. Kreuz, *J. Am. Chem. Soc.*, **72**, 5543 (1950); H. Wynberg and A. Logothetis, *J. Am. Chem. Soc.*, **78**, 1958 (1956).

(4) J. Teste and N. Lozach, *Bull. soc. chim. France*, 492 (1954); H. Wynberg, A. Logothetis, and D. VerPloeg, *J. Am. Chem. Soc.*, **79**, 1972 (1957).

tion, the formation of thianaphthene and the phenylthiophenes could be visualized as follows:



Since it is known⁵ that acetylene will react with sulfur and hydrogen sulfide to furnish, among other products, the thiophthenes, the above scheme could form the basis for most of the products found in the pyrolyzate. It is clear that route A provides for the formation of dibenzothiophene while route B would furnish 3-phenylthiophene if 2,3'-bithiophene or, better 3,3'-bithiophene were the diene.

EXPERIMENTAL

Thiophene⁶ (150 g.) was heated to 60-65° and passed through a 90 × 1 cm. Vycor tube at a rate of 5 ml. per hr. with the aid of a slow stream of dry nitrogen. A tube oven maintained 50 cm. of the Vycor tube at 800-850°. A series of cold traps (Dry Ice) was used to collect the pyrolyzate. Hydrogen sulfide was collected as lead sulfide. When all of the thiophene had been swept through the system (31 hr.), the contents of the traps, 143.7 g., were distilled. A forerun of 8.7 g. (15%)⁷ of carbon bisulfide, b.p. 35-45°, was followed by 89.7 g. (60%) of unreacted thiophene, b.p. 69-85°. Steam distillation of the residue furnished 8.2 g. (13.6%)⁷ of steam-volatile material leaving 20 g. (34%) of residue. The steam-volatile fraction was separated into 3.09 g. of an oily fraction, IA, and 4.45 g. of a crystalline fraction, IB, by sublimation at 40-60° (0.3 mm.). The mass spectrum of these fractions is shown in Table III.⁸

TABLE III
MASS SPECTRUM

Structure	Mass	%	
		Fraction IA	Fraction IB
	128	6	
	134	60	2
+ isomers	140	4	
+ isomers	160	2	8
+ isomers	166	25	85

(5) H. D. Hartough "Thiophene and Its Derivatives," Interscience Publ., Inc., N. Y., 1952, p. 49; see also W. E. Parham and P. L. Stright, *J. Am. Chem. Soc.*, **78**, 4683 (1956) for the elimination of acetylene from vinyl sulfides.

(6) Generously donated by The Texas Co.

(7) These percentages are based on the 60. g. of thiophene actually converted.

TABLE IV

INFRARED ABSORPTION BANDS FOR BITHIOPHENES

2,2'-Bithiophene	3,3'-Bithiophene	2,3'-Bithiophene
3.25 m μ	3.25 m μ	3.25 m μ
5.56	6.44	5.56
6.07	6.64	6.07
6.26	6.93	6.44
6.64	7.12	6.64
6.91	7.46	6.95
7.08	8.00	7.11
7.40	8.22	7.24
7.55	8.36	7.50
8.09	8.50	8.01
8.29	9.20	8.13
8.49	9.58	8.36
8.65	9.95	8.52
9.25	10.24	9.22
9.56	11.44	9.55
10.92	11.83	9.94
11.16	13.08	10.06
11.7-12.4	14.36	10.20
13.44	14.64	11.40
14.0-14.8		11.68
		11.90
		12.13
		12.52
		12.95
		14.40
		14.96

The crystalline fraction IB was subjected to fractional crystallization and chromatography as follows: One g. of IB was crystallized from 15 ml. of absolute methanol. The crystalline material thus obtained melted at 82-93°. After six crystallizations there was obtained 15 mg. of pure 3,3'-bithiophene, m.p. 132-133°, undepressed on admixture with an authentic sample.⁹ Liquid crystal formation of pure 3,3'-bithiophene appears to occur at 115-122°.

Concentration of the mother liquor from crop I to one half its volume furnished an intermediate fraction, melting at 52-80°. This fraction (100 mg.) was chromatographed

(8) All spectra were determined by Dr. G. D. Hinds, Jr., Chief Research Technologist and his associates of the Houston Research Laboratory of the Shell Oil Co.

(9) Prepared in 10% yield by the method described by Auwers and Bredt.

TABLE V

ULTRAVIOLET ABSORPTION MAXIMA FOR DITHIOPHENES

Compound	EtOH max m μ	E $\times 10^{-4}$
2,2'-Dithiophene	301	1.30
	263 (min.)	0.38
2,3'-Dithiophene	246	0.60
	283	1.19
	250 (min.)	0.52
3,3'-Dithiophene	235	0.84
	260	1.13
	240 (min.)	0.48
	230	0.9-1.0

over 11.2 g. of basic alumina.¹⁰ Using petroleum ether (distilled, b.p. 34-38°) as the eluant, fractions of 20 ml. each were collected. In this manner fractions 9, 10, and 11 melting at 50-57.5° were combined and recrystallized 3 times from petroleum ether (b.p. 34-38°) furnishing shiny platelets, m.p. 61.5-63.0°. A mixture m.p. with authentic 2,3'-bithiophene (m.p. 60.5-61.0°) was 60.8-62.8°.

All fractions melting below 50° were combined and recrystallized from petroleum ether. In this manner a small amount (less than 2 mg.) of material melting at 42-44° was obtained (2-phenylthiophene is reported to melt at 37° and 43°¹¹). Concentration of the mother liquors furnished an oil, which was dissolved in glacial acetic acid. Dropwise addition of a solution of bromine in glacial acetic acid at room temperature resulted in rapid crystallization of 5,5'-dibromo-2,2'-bithiophene as shiny flat plates m.p. 137-140.5°. One recrystallization from methanol furnished the pure dibromide m.p. 146-147.6° as colorless glistening platelets. On admixture with the dibromo compound (m.p. 146.8-148.0° prepared in exactly the same way from authentic 2,2'-bithiophene¹²) the melting point was not depressed.

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(10) "Woelm" alumina, activity grade I.

(11) Ref. 5, p. 477; J. L. Melles and H. J. Backer, *Rec. trav. chim.*, **72**, 314, (1953).

(12) Prepared most conveniently by heating a mixture of 2-bromothiophene (66 g.), copper-bronze (66 g.), and 66 ml. of dimethylformamide under reflux for 100 hr. followed by steam distillation. The preparation of 2,2'-dithiophene from 2-bromothiophene has not been reported previously.